SCIENTIFIC PAPERS

OF THE

BUREAU OF STANDARDS

VOLUME 19

Nos. 469-497

APPLICATION OF THE INTERFEROMETER TO MEASUREMENTS OF THE THERMAL DILATATION OF CERAMIC MATERIALS.

By George E. Merritt.

ABSTRACT.

An interference method and apparatus for measuring the thermal expansion of ceramic materials are described. The samples in the form of tripods or small pins, 0.5 to 10.0 mm in length, are placed between two fused quartz interferometer plates and heated in an electric furnace. The elongation of the sample is determined from the number of interference fringes that pass reference marks on the upper interferometer plate. Measurements made on the thermal expansion of several samples of glaze, terra cotta, tile, porcelain, and clay show that this method gives accurate and reproducible results. These, represented by curves, show that the expansivities of different ceramic materials may differ greatly; that the expansion of a given material may be different at different parts of the temperature scale; and that some materials may undergo permanent dimensional changes when subjected to heat treatment. They also serve to explain why some materials fail and others do not when subjected to the same treatment and emphasize the need of accurate data on expansivity of each material if it is to be subjected to sudden temperature changes when combined with another material differing in composition.

CONTENTS.

I. INTRODUCTION.

The dimensional change with variation in temperature determines, to a large extent, the behavior of ceramic materials during the process of manufacture and also affects the quality, durability, and resistance of the finished product.

When clay products, such as terra cotta, tile, porcelain, etc., are cooled rather quickly in the furnace, cracks may develop arising from the outer layer contracting at a different rate than the inner

mass, which is at a higher temperature. If more than one material is used (as in the case of glazed ware), the expansivities of the materials should be identical below the annealing range of the material possessing the lower one, or strains are likely to be set up during cooling which later produce cracks in the glaze, and may even cause it to scale off. Accurate data on the expansion over the entire working range of temperature is essential for the best choice and manipulation of the materials.

The present investigation was undertaken for the dual purpose of proving the applicability of the interference method to this problem, where it is often necessary to work with very small samples of the material, and at the same time of determining the thermal expansivity of some ceramic materials over a large temperature range. Measurements were made on several different samples of glaze, tile, porcelain, and terra cotta in the temperature interval 20 to 950° C. The effect of heating the sample at different rates and of taking it over the same range several times was also investigated.

II. EXPERIMENTAL METHOD.

1. FIZEAU METHOD.

The interference method as originated by Fizeau[1] and later developed by Pulfrich[2] was particularly adapted to this work because the extreme sensitiveness of the interferometer makes it possible to work with a small specimen of the material, and because the small size of this apparatus simplifies the problem of uniform heating and temperature control. By this method the change in length of a ring or tripod of the material used as a separator for the interferometer plates is determined from the shift of the straight interference fringes past a reference mark ruled in the center of the lower surface of the upper plate. These fringes produced by interference of the light reflected from the interior faces of the two interferometer plates are observed with a Pulfrich[3] apparatus. Any elongation or contraction $\pm\Delta L$ in the length, L, of the specimen which forms a separator for these two faces causes a corresponding movement of the interference fringes past the reference mark.

In passing from one temperature t, with the plates at a distance apart equal to L, to a second temperature $t + \Delta t$ with the plates at

[1] Fizeau Ann. d. Phys., 128, p. 564; 1866.
[2] Pulfrich Zeits. f. Instrk., 13, p. 365; 1893.
[3] C. Pulfrich Zeits. f. Instrk., No. 9; 1898.

a distance equal to L + ΔL, a band passes the reference mark each time the total number of wave lengths in the path (double distance) increases by one. The number of bands ΔN that pass is then obviously equal to the difference in the number of wave lengths in the double distance under the two conditions. If λ represents the wave length of the light then

$$\Delta L = \frac{\lambda \Delta N}{2} \qquad (1)$$

and the mean coefficient of expansion

$$C = \frac{\lambda \Delta N}{2L\Delta t} \qquad (2)$$

Since the observations are made at the reference mark, the quantity ΔL is the change in the distance between the two plates at that point, and this is equal to change in length of the three corners of the tripod, providing their behavior is identical; otherwise it approximates their mean elongation if they behave differently.

2. THREE-PIN METHOD.

In a further modification of the interference method developed by Peters [4] three entirely separate pins are used as separators for the plates instead of a tripod or ring. The pins are made in the form of cones, about 4 mm across the base and from 2 to 10 mm in height. The exact change in length of each individual pin is determined from the number of fringes that pass the point of contact of that pin with the upper plate. The advantages of this modification are that extremely small samples can be used, and three samples from different specimens or from different parts of the same specimen can be investigated simultaneously.

III. DESCRIPTION OF APPARATUS.

1. INTERFEROMETER AND SPECIMENS.

The two plates *A* and *B* of the interferometer represented in Figure 1 were made of fused quartz, which can be heated to 1,000° C. without serious injury to the surfaces. The upper surface of the base plate *B* was polished true plane, while the lower surface was left in the ground condition to eliminate reflection therefrom. Both surfaces of *A* were polished true plane,

[4] Peters, Jour. Wash. Acad. Sci., 9, No. 10, p. 281; 1919.

making an angle of about 20 seconds with each other, so that light reflected from the upper surface could be diaphragmed out of the field of view. The separator *S*, the test piece or pieces, consisted either of a triangle of the porcelain or other clay with feet at the corners and a hole in the middle through which to view the fringes, or of three separate fragments or pins of the material to be tested.

In case the individual expansions of the pins are to be measured, it is important that the shadow outline of each pin be small and round, or at least regular in form, and that the point of contact with the upper plate be in the center of this shadow, because this locates the point of contact which can not itself be seen. Where an average of three samples is to be taken from readings on a central reference mark *R*, these may be of any shape, even rough fragments, the requisites being that each stand solidly alone; that all have practically equal lengths; and that their points of contact with the upper plate be about the same distance from the reference mark. Where heating is to be rapid, they should also be of nearly equal mass.

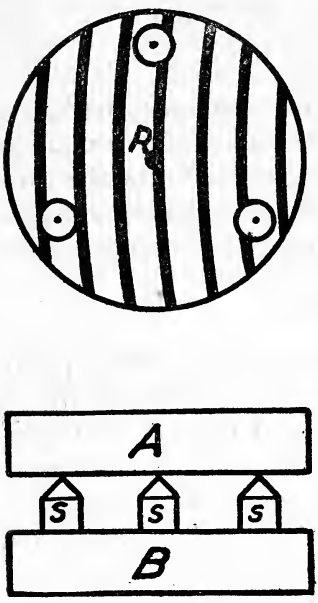

FIG. 1.—*Interferometer.*

2. FURNACE.

A sectional view of the electric furnace containing the interferometer is given in Figure 2. A porcelain tube *F*, 5 cm in diameter and 30 cm long, wound spirally with a heating coil *K*, is mounted vertically in a sheet-iron jacket and surrounded with insulating material. A smaller procelain tube *E*, which extends from the base to about 3 cm from the center of the furnace, supports the porcelain disk *D*, the space below this disk being filled with an insulating material. A porcelain cup *C*, with a cover *H*, acts as a container for the interferometer *A S B* and can be lowered into the furnace by a platinum wire until it rests on the disk *D*. A small double-bore porcelain tube containing the thermocouple *T* passes through the base of the furnace, the disk *D*, and the bottom of the cup *C*, the thermocouple junction being adjusted so that it nearly touches the lower interferometer plate B. The upper end of the furnace tube is closed by another

porcelain tube containing the fused quartz windows W_1 and W_2, while W_3 is a glass window in a sheet of asbestos board.

The Pulfrich apparatus, using the yellow radiation from helium for illuminating the interferometer and an optical arrangement for measuring the displacement of the fringes, is represented by P.

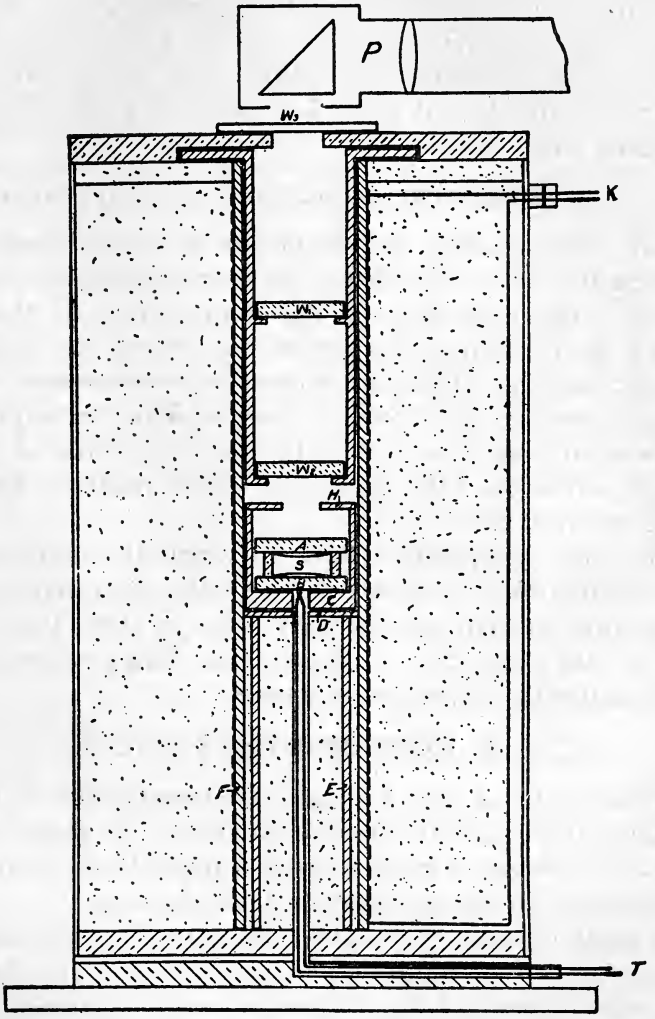

FIG. 2.—*Electric furnace.*

The heating coil K, which has a resistance of 17 ohms, is designed to operate on a 110-volt circuit with an ammeter and suitable rheostat to regulate the current. A current of 4 amperes is sufficient to heat the furnace from room temperature to 700° C. at the average rate of about 4° C. per minute.

IV. EXPERIMENTAL PROCEDURE.

1. OPTICAL ADJUSTMENTS.

The sample having been prepared in the shape of a tripod, or the three samples for the separate pins having been selected and reduced to similar shape, the distance between bearing points of the two ends of each is carefully measured with a micrometer. When these measurements show equality, the specimen is inserted between the interferometer plates, and the resulting fringes brought to the desired width by abrasion of one of the contact points on a dry oilstone.

2. TEMPERATURE REGULATION AND OBSERVATION.

The heating current was regulated to a very nearly constant temperature rate throughout the run—usually 2.5 to 3° per minute. The expansion of the sample, due to this heating, caused the interference fringes to move across the field, and the number that passed the reference mark were counted. Starting at room temperature (20° C.), thermocouple indications of the temperature were observed at the moment of transit of definite fringes across the reference mark. Such readings were usually made on every fifth fringe.

The upper temperature limit to which the different samples were heated ranged between 600–970° C. On reaching this limit the heating current was reduced so as to allow the samples to cool at the same rate. Observations during contraction were made as during the heating process.

V. EXPERIMENTAL RESULTS.

Figures 3 to 14 give a graphical representation of the results obtained from various selected materials. In these the elongation ΔL of samples 1 cm in length are plotted as ordinates and the temperature (in degrees centigrade) as abscissas.

In many of these curves the slope is neither constant nor constantly increasing, and in both clays and glazes the changes may be abrupt. Many of the clays show sudden increases in the rate of expansion in the neighborhood of 575° C. These are probably due to the $\alpha \rightleftarrows \beta$ quartz transformation which occurs at this temperature. In the case of the glazes (that is, glasses), however, the increase in the rate of expansion which takes place anywhere between 300 and 700° C. is due to some readjustment always related to the softening of the material. As in the case of true

glass, the temperature where the rapid increase in expansion begins is within the annealing range, and below this temperature any deformation in the glaze practically ceases.

Figure 3 represents the average heating and cooling curves of three samples (11 mm in length) taken from a terra-cotta tile. It exhibits the usual relation between the heating and cooling curves which for fully matured ware are similar in shape and parallel to each other. For the purpose of matching *bodies* with *glazes* it shows that heating curves may be used with as much confidence as cooling curves.

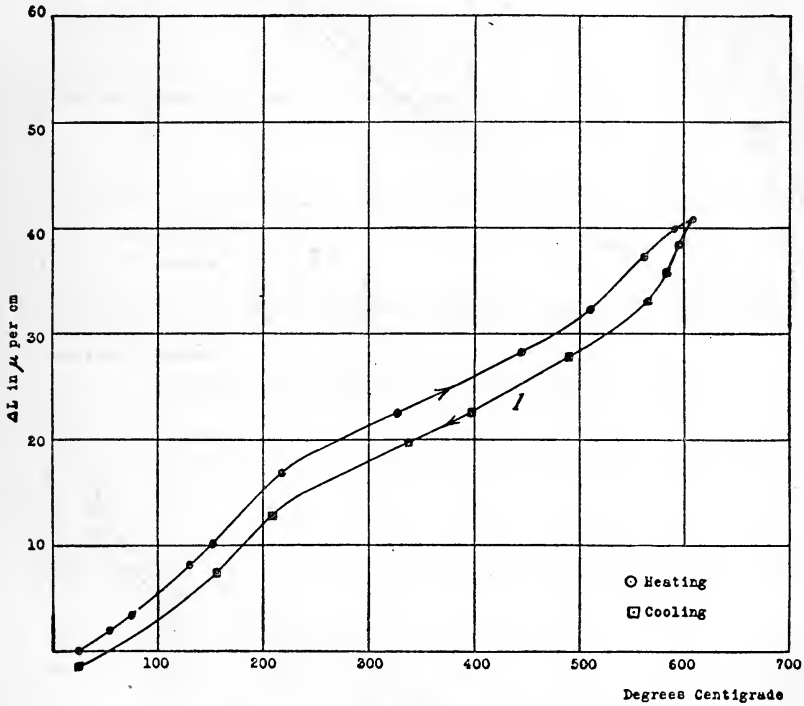

FIG. 3.—*Thermal dilatation of terra-cotta tile.*

Figure 4, curve *2*, shows the expansion of a terra-cotta brick and curve *3* the expansion of its glaze. This glaze seemed to be in good condition, but on being heated to 125° C. and plunged into cold water (20° C.) it crazed immediately. This was caused by the strains introduced, due to the difference in expansivities of the materials when initially cooled from the temperature where the glaze became hard, and also by the very different rate of expansion and contraction that exist in the region of sudden quenching. The data for these curves was obtained from specimens of the material 0.41 mm long chipped from a finished tile.

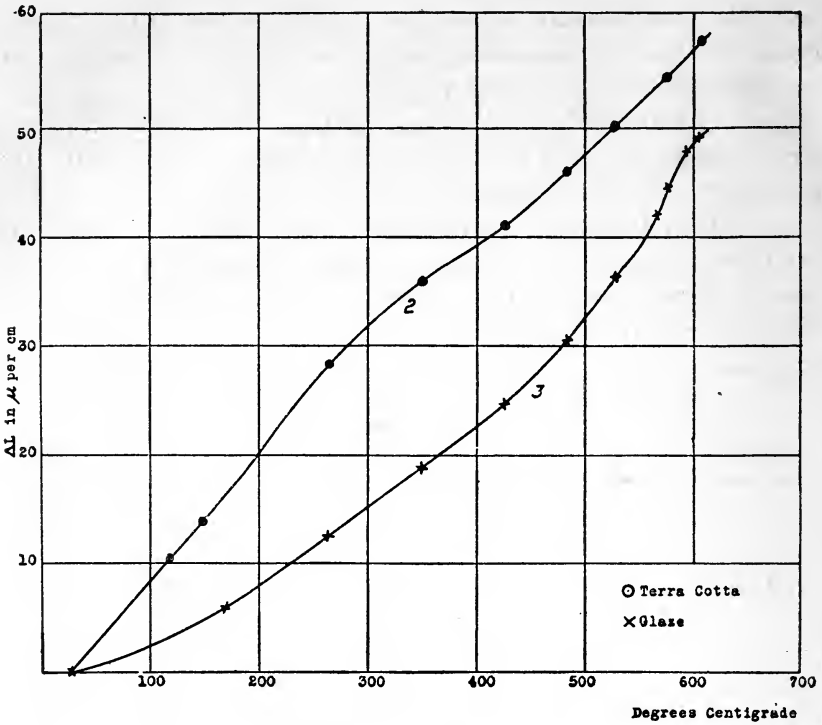

FIG. 4.—*Thermal dilatation of terra-cotta tile and glaze.*

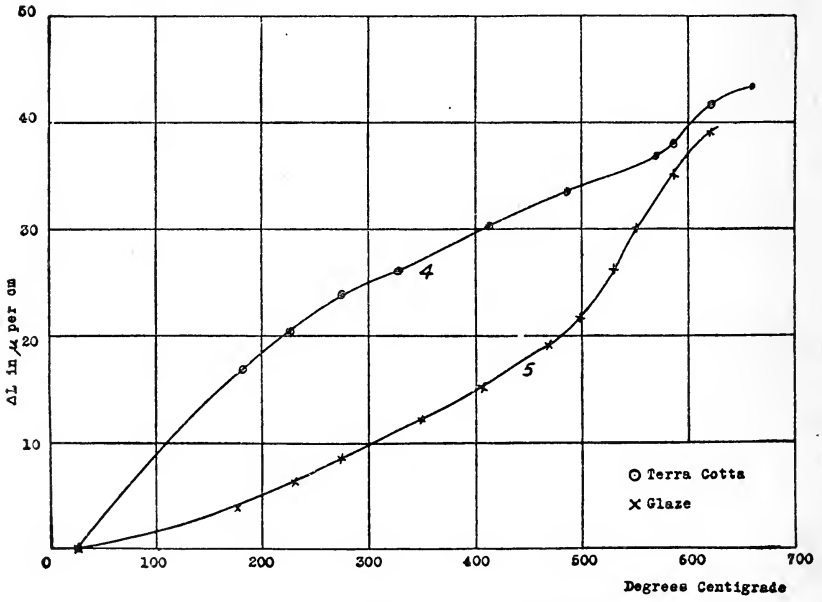

FIG. 5.—*Thermal dilatation of terra-cotta tile and glaze.*

Figure 5 represents the expansion of other samples of tile and glaze 0.37 mm in length taken from the same brick from which the sample of Figure 4 was taken. The same differences in the expansivities of tile and glaze are shown by both sets of samples.

The differences between the two expansion curves of the glaze or tiles are not due to inaccuracies of measurement, as each curve is the average of two runs on the same samples, and differences between the individual observations were much less than differences between the results for the two samples.

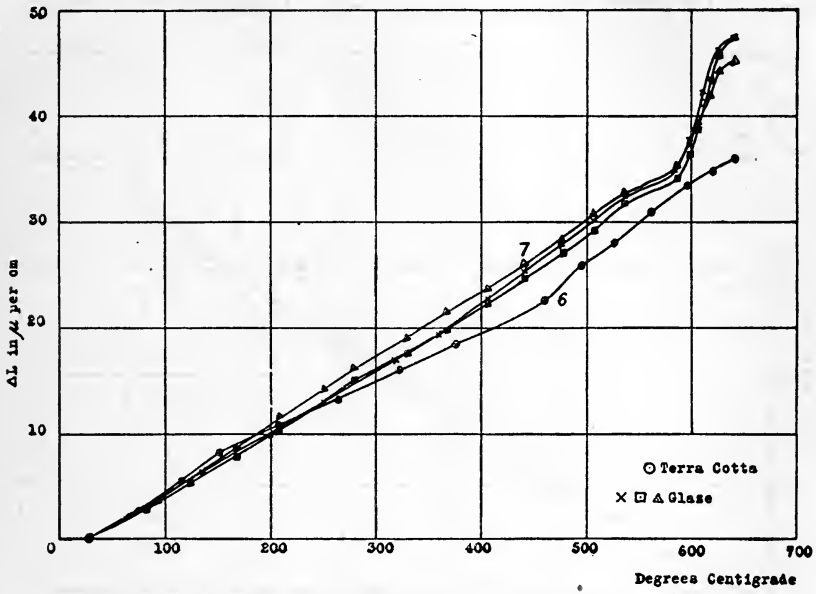

FIG. 6.—*Thermal dilatation of architectural terra-cotta tile and glaze.*

Figure 6 shows the expansion curves of a glazed architectural terra-cotta ornament. Curve *6* for the terra cotta was obtained from three fragments of 12.03 mm in length. The three samples of glaze were each 1.27 mm in length, and their expansions were measured individually by the three-pin method. Although these curves for tile and glaze seem to match at lower temperatures there is a marked divergence in the region above 600° C. This specimen failed in use, the glaze crazing badly and the body crumbling on exposure to the weather. Possibly slower cooling in the region near 600° would have prevented the failure, as this would have given the glaze a chance to anneal. This figure is a good instance of a pair of materials which seem to match when only the lower part of the expansion curve is known, but exhibit marked divergence at higher temperatures.

Figure 7 shows the results from a terra-cotta brick and its glaze which stood the quenching test exceptionally well. Ware made out of these materials was heated to 125° and then plunged into cold water. No crazing was visible until after the fifth repetition of this treatment. The curve for the glaze represents the average expansion of three samples 0.44 mm in length chipped from a tile. The three fragments of the body 9.95 mm long were broken from the same tile. These curves illustrate the agreements of the expansivities of body and glaze that make a product that will be permanent and resist sudden temperature changes.

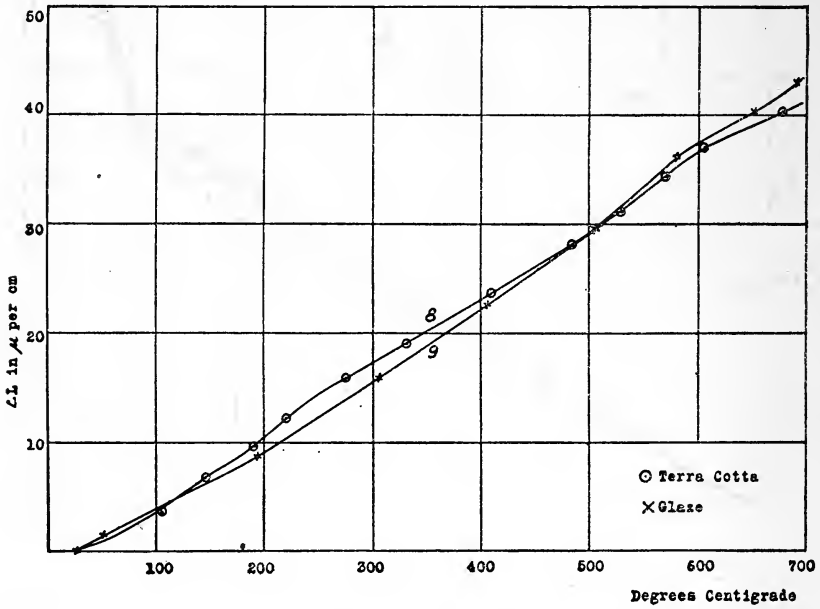

FIG. 7.—*Thermal dilatation of terra-cotta tile and glaze.*

Figure 8 represents the thermal expansions of two different glazes of unknown composition. Curve *11* is the result of observations on samples of 0.48 mm long taken from a finished specimen, while curve *10* was obtained from three lumps of glaze material 6.95 mm long. They show the applicability of the method to small samples in that the results of observations on the small specimens are as regular as those of the longer.

The curves of Figure 9 represent the thermal expansions of two samples 1 cm in length cut from the same hollow tile, curve *12* representing the expansion perpendicular to the direction of flow and curve *13* that parallel to the direction of flow.

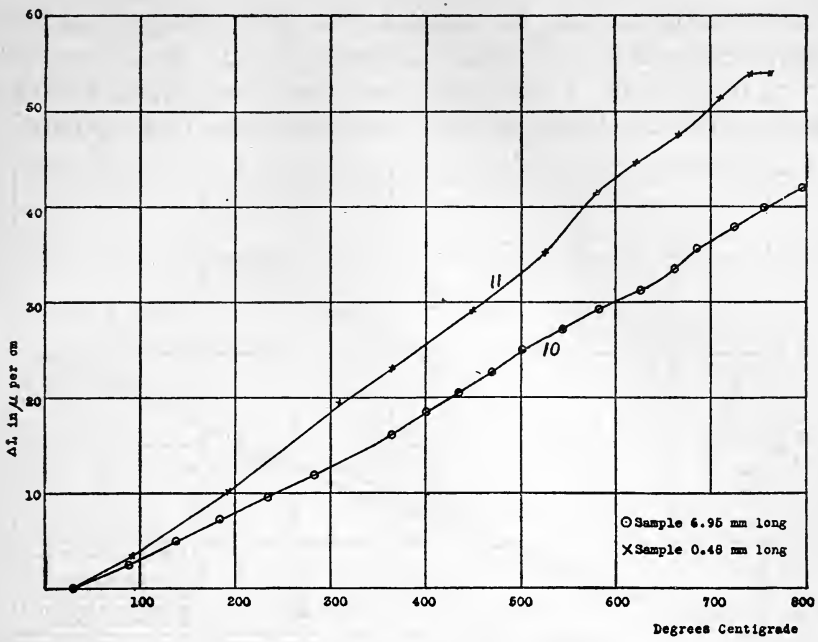

FIG. 8.—*Thermal dilatation of glaze.*

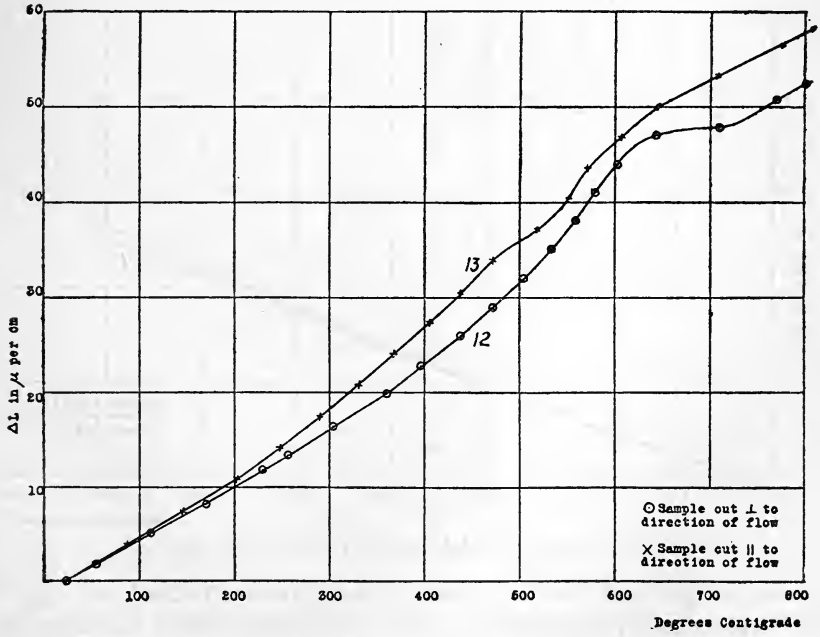

FIG. 9.—*Thermal dilatation of hollow tile.*

Observations made on samples from four different kinds of clay are shown in Figure 10. Curves *14* and *15* show the results from, respectively, a first and second run on a sample of Florida kaolin, which exhibits in both cases the same rapid expansion

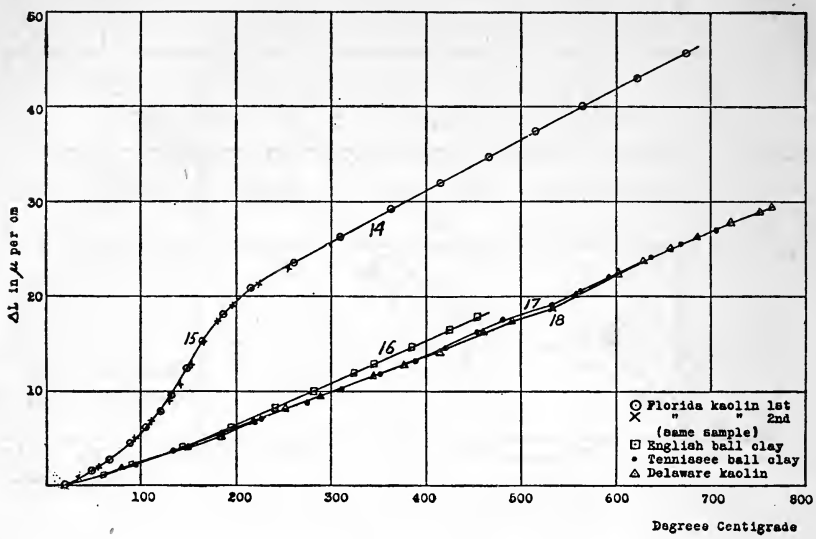

FIG. 10.—*Thermal dilatation of four samples of clay.*

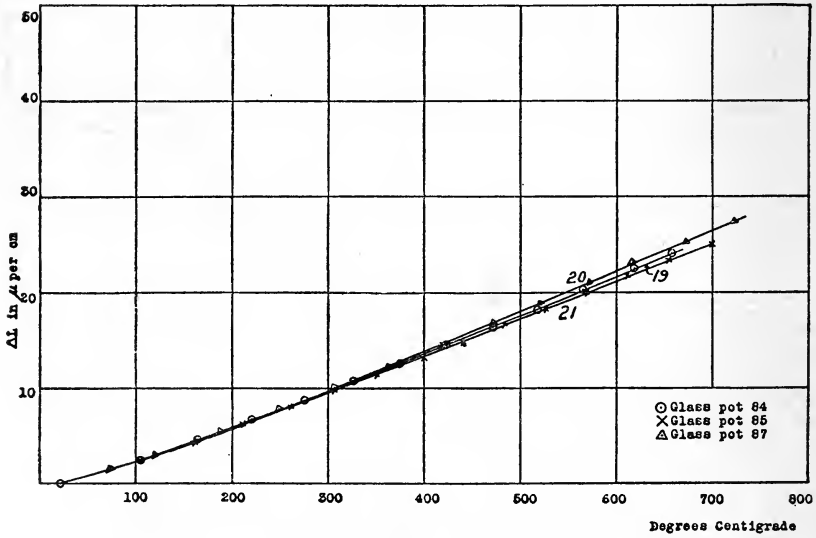

FIG. 11.—*Thermal dilatation of optical glass pots.*

between 100 and 200° C., and which does not exist, in any of the other clays (curves *16*, *17*, and *18*). This effects seems to be, therefore, a permanent characteristic of the expansion of this material, which is not affected by heating to 700° C.

The curves of Figure 11 represent the thermal expansions of three fragments taken from each of three pots in which optical glass has been melted.

The following table gives the batch analysis of these pots:

TABLE 1.—Batch Analysis of Bureau of Standards Glass Pots.

Material.	Samples—		
	84	85	87
	Per cent.	Per cent.	Per cent.
Feldspar	6	4	4
Tennessee ball clay	10	16	16
Kentucky ball clay	10	9	9
Kaolin	21½	21	21
Grog[1]	52½	50	50

[1] Grog: 50 per cent Tennessee ball clay, 50 per cent kaolin.

Samples 85 and 87 are of the same composition, but 85 was cooled rapidly and 87 very slowly after the glass was melted. The cooling rate of 84 lay between the rates of the other two. With all three pots the three samples taken from each pot were found to have very nearly identical expansion, thus indicating that a homogeneous mixture had been obtained.

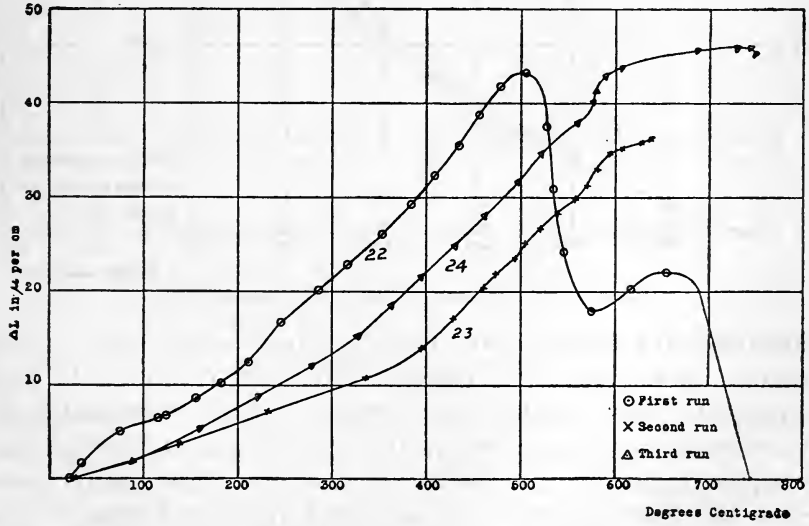

FIG. 12.—*Thermal dilatation of unburned clay.*

Figures 12, 13, and 14, represent the mean results obtained from eight consecutive runs on the same three samples of unburned clay, illustrating successive changes in the material due to heating. These samples were in the shape of cones rounded at the top and almost as wide as high. Their length when green

was 9.53 mm after drying at room temperature. With exception of the fourth and fifth runs all were heated at 2.5° per minute. The crook in curve *22*, representing the first run, beginning at 90° and continuing for some distance above 200°, does not reappear in any of the subsequent heatings and is probably connected with the liberation of moisture by the green samples. Above 500° C., which is the temperature at which kaolin begins to lose chemically combined water, all three specimens began to shrink rapidly, the interference fringes becoming very narrow due to the unequal contraction of the three pins, making it very difficult to count the number of fringes that passed the reference mark. The values given above 500° are, therefore, only a close approximation. Near 575° the expansion began again and con-

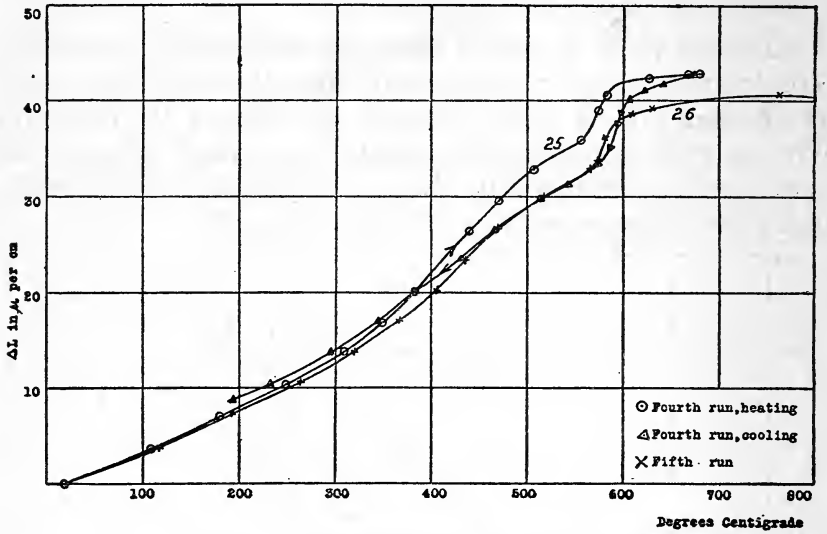

FIG. 13.—*Thermal dilatation of unburned clay.*

tinued up to a temperature of 660° C., from which point on contraction took place at a uniform rate. On returning to room temperature the samples were measured with a micrometer and found to be 9.45 mm in length, the heat treatment having shortened them 0.08 mm, or about 0.8 per cent. The samples were again adjusted (length 9.40 mm) and replaced in the furnace for further examination. Curve *23*, Figure 12, shows the results of a second run. In this run they were heated to 650° C.without any contraction taking place. An appreciable increase in the expansion occurred between 560 and 600° C., which is the region of the second expansion during the first run. A more marked increase in the expansion occurred during the third run (curve *24*) on passing through the same temperature region. Above

600° the rate decreased, and at 750° contraction began. Curve *25* of Figure 13 represents the results obtained during both heating and cooling of the fourth run in which the samples were heated at the rate of 3.7° C. per minute and cooled at 2.6° C. per minute. Curve *26* gives the results of a fifth run when the heating rate was 2° per minute. The three curves obtained from the third, fourth, and fifth runs are very similar, showing an increase in the rate of expansion near 350° C., another at 560° C., and a rapid decrease above 600° C.

Curve *27*, Figure 14, represents the results of a sixth run in which the samples were carried up to 970° C. Up to 806° C.,

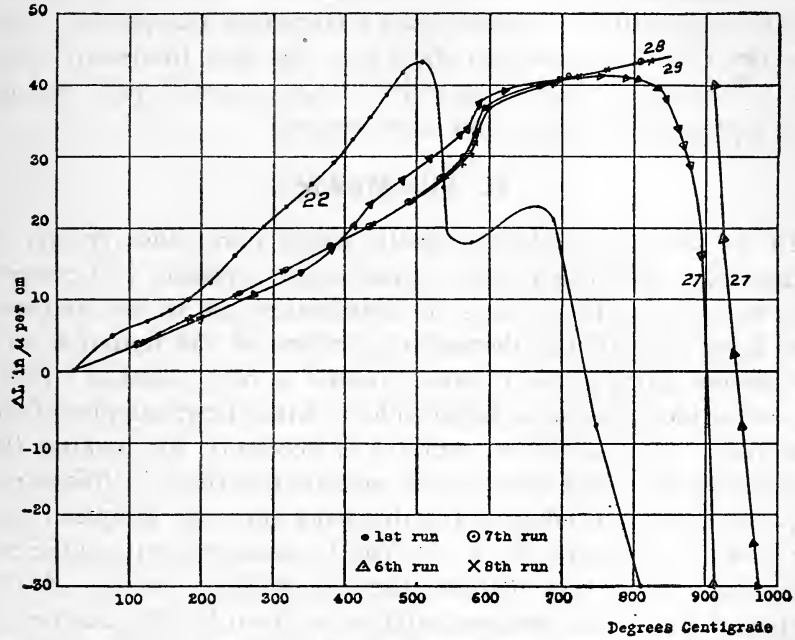

FIG. 14.—*Thermal dilatation of unburned clay.*

which was the highest temperature that had previously been reached, it has the same form as the curves from the three preceding runs. Between 806 and 970° C., the samples shortened rapidly. This shortening was similar in effect to that which occurred above 500° during the first run. After being held at 970° C. for a half hour and then cooled to room temperature the samples measured 9.24 mm in length as compared with the initial value of 9.40 mm, showing a permanent shrinkage of 0.16 mm, or 1.7 per cent.

The results of the seventh and eighth runs are represented by curves *28* and *29*, Figure 14. These are almost identical, but

differ from any of the preceding ones. No shrinkage occurred at 850° nor any change in the expansion at 350°. The rapid increase in expansion between 560 and 600° C. was, however, still present. This increase is very similar in its effect on the expansivity to that of glass on passing through its "critical region."

With the reproduction of curve *22* on this plot the curves of Figure 14 summarize the results obtained from this clay. Curve *22* represents the first run (on the green clay) and shows the rapid contraction between 500 and 806° C. The part of curve *27* below 800°, which is typical of the curves obtained from the second, third, fourth, fifth, and sixth runs, shows contraction had been eliminated by this first heat treatment. On heating to still higher temperatures, however, the contraction reappeared. The last two curves (*28* and *29*) show that the heat treatment up to 970° C. had made the expansivity of the material quite regular and reproducible below this temperature.

VI. SUMMARY.

In the making of clay products, which may differ greatly in composition and which must stand large variation in temperature both during the process of manufacture and in use, an accurate knowledge of the thermal expansions of the materials and of different parts of the finished product is very essential. Since it is often inconvenient or impossible to obtain large samples of the material, a very sensitive method is necessary for making the measurements. The interference method described in this paper is particularly well adapted for this work, because samples ranging in length from 0.5 to 10 mm can be measured with sufficient accuracy. With this method the dimensional change of the samples for any temperature interval is given by the number of fringes, produced by the yellow radiation from a helium source, which pass a reference mark on the front interferometer plate.

In order to show the need of accurate knowledge of the expansion and prove the applicability of the interference method, observations were made in the temperature region between 20 and 970° C. on a variety of ceramic materials consisting of several different samples of glaze, terra-cotta, tile, porcelain, glass pots, and unburned clay.

The results of this investigation show that different ceramic material may differ greatly in expansivity; that the expansivity of a given material may be very different at different parts of the

temperature scale; and that a material may undergo permanent dimensional changes when subjected to heat treatment. The need for extensive measurements on the expansion of each material is therefore apparent. The consistency and reproducibility of the results obtained on seasoned samples, even when they are less than 1 mm in length, and the facility with which measurements can be made over a temperature interval of 1,000° C. shows that the interference method is sufficiently accurate for making the measurements and particularly well adapted for studying the homogeneity of any given mass.

WASHINGTON, September 28, 1923.